PB83-192245

Methods 6 and 7 Quality Assurance and Quality Control Revisions - Background Information

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Dec 82

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/3-82-017
December 1982

Air

PB83-192245

EPA

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1. REPORT NO. EPA-450/3-82-017	2.	3. RECIPIENT'S ACCESSION NO. PB83 192245
4. TITLE AND SUBTITLE Methods 6 and 7 Quality Assurance and Quality Control Revisions - Background Information		5. REPORT DATE December 1982 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Emission Standards and Engineering Division		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Emission Measurement Branch (MD-19) Emission Standards and Engineering Division U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS DAA for Air Quality Planning and Standards (MD-19) Office of Air, Noise, and Radiation U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document serves as background information for the proposed revisions to Methods 6 and 7. Data are included to substantiate the recommended revisions and information is provided to aid testers in minimizing analytical inaccuracies.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
		13B

18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21.
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-450/3-82-017

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Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1982

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METHODS 6 and 7 QUALITY ASSURANCE AND QUALITY CONTROL REVISIONS

BACKGROUND INFORMATION

Introduction

Methods 6 and 7, the Quality Assurance Handbook,[1] and data from the Environmental Protection Agency (EPA) audit surveys were reviewed to determine whether additional quality assurance and quality control procedures should be added to Methods 6 and 7. For both methods, the Handbook recommends the use of (1) a performance audit of the analytical phase and (2) an audit of the data processing. The Handbook also recommends a 7-percent accuracy limit (chosen at the 90th percentile level) for Method 6 and a 20-percent accuracy limit (chosen at the 80th percentile level) for Method 7. These criteria for acceptability of analytical audit results were based on summarized data received from various laboratories participating in the EPA audit survey program.[2,3]

Past experience indicates that increased familiarity with the methods (especially Method 7) tends to increase operator accuracy. Since the acceptability limits recommended by the Quality Assurance Handbook for the audit analyses were thought to be excessive, the audit surveys were evaluated to determine the causes for the high levels of inaccuracies. This document summarizes the findings and makes recommendations for minimizing analytical inaccuracies.

Results

The data obtained from EPA Audit Surveys 0980 and 0281 for SO_2 and Surveys 0480, 1080, and 0481 for NO_x were evaluated. Survey 0481 for NO_x included data on the calibration curves as well as the audit results. Four sources of errors were isolated as follows:

1. Reporting.
2. Calculation.
3. Analytical bias.
4. Poor analytical precision.

These types of errors are summarized in Table 1 and illustrated in Tables 2 through 6.

In Table 1, the following criteria (after analytical bias correction) were used to determine poor analytical precision for the audit survey data:

1. Method 6 audits: Two or more out of five results greater than 5 percent error.
2. Method 7 audits: Three or more out of five results greater than 10 percent error.
3. Method 7 calibration curve: Two or more out of four standards greater than 7 percent deviation from the least squares line.

Table 2 shows an example of a reporting error. The last two reported values were apparently interchanged. After these values were changed back to the proper order, the percent differences were recalculated to be -1.4 and -2.8 percent instead of -67.6 and 196.7 percent, respectively.

Table 3 illustrates two types of calculation errors. The first example indicates that a factor of 2 was introduced; therefore, the reported values were doubled and the percent differences were recalculated to the values shown in the table. Factors of 2 and decimal point errors were the most common calculation errors. These errors generally result from using the wrong aliquot factor or, as in the case of SO_2, using the wrong normality for the barium standard.

The second example in Table 3, a less common type of error, indicates that there was an average difference of -242.4 between the EPA and reported values. This average difference was added to the reported values and the percent differences were recalculated to the values shown in the table.

Table 4 provides examples of results with analytical biases, and Table 5 is an example of results with both a calculation error and analytical bias. The results with analytical biases showed good precision, but poor accuracy. These errors generally come from the incorrect preparation of the potassium nitrate or barium standards. Although constant percentage differences could be attributed to the use of a wrong constant (e.g., wrong molecular weight) in the calculation, they were all classified as analytical biases.

Table 6 presents examples with poor analytical precisions in calibration and audit analysis. Laboratories with poor analytical precision cannot be expected to analyze samples correctly.

Table 7 summarizes the data from the audit survey after correction of reporting and calculation errors and mathematical adjustment of

the results for analytical biases. The data were treated in two ways. First, all analyses were considered. Second, the results of laboratories exhibiting poor analytical precision were deleted from the total. For Survey 0481 (NO_x), a third analysis was performed on the results of only those laboratories having calibration curves with good precision.

Discussion and Conclusions

Table 1 shows that the majority of the errors come from analytical biases; other errors resulted from poor analytical precision and calculation mistakes. Since these errors are correctable with appropriate quality control techniques, the audit survey data could be salvaged. Analytical biases were adjusted, reporting and calculation errors were corrected, and results from laboratories with poor analytical precision were deleted. Table 7, a summary of the data after correction, serves as a good indicator of laboratory capabilities.

Table 7 shows that after the results of poor analytical precision were deleted and other errors were corrected, 97 percent of the total number of SO_2 analyses were within 5 percent of the EPA audit concentration, and over 90 percent of the total NO_x analyses were within 10 percent of the EPA audit concentration. Even without deleting the results of poor analytical precision, 96 percent of the total SO_2 analyses were accurate to within 5 percent for Survey 0281, and 91 percent of the total NO_x analyses were accurate to within 10 percent for Survey 0481. These surveys were conducted in February and April

of 1981, respectively, and showed an improvement from the previous surveys, e.g., 93 percent for SO_2 Survey 0980 and 85 and 83 percent for NO_x Surveys 0480 and 1080, respectively.

When the above figures are compared to the criteria recommended in the Quality Assurance Handbook (7 percent for SO_2 and 20 percent for NO_x), Table 7 shows that analytical laboratories are able to meet more stringent limits. Table 7 also shows that the Quality Assurance Handbook's recommendation to analyze audit samples simultaneously with Methods 6 and 7 samples must be instituted to encourage accurate analyses.

Recommended Quality Control/Quality Assurance Procedures

As mentioned earlier, analytical biases, poor analytical precision, and calculation errors can be corrected with appropriate quality control techniques. The direct approach would be to first run the analyses using standard solutions until an acceptable precision is obtained. Then the second step would be to check the results against an accepted standard (certified samples) and remove any analytical biases or calculation errors.

The following quality control/quality assurance procedures and criteria are recommended to minimize inadequate analytical techniques, calculation errors, and analytical biases:

1. Establish analytical precision.

a. Method 6: Using the sulfuric acid standard solution, run triplicate analyses. The titrations should agree within 1 percent or 0.2 ml, whichever is larger.

b. Method 7: Using the calibration curve data, multiply the least-squares constant, K_c, by the absorbance. All four standards should agree within 7 percent of the standard concentrations, i.e., 100, 200, 300, and 400 µg NO_2.

2. Eliminate analytical biases and calculation errors.

To accomplish this, obtain SO_2 and NO_x samples with known concentrations from EPA or other reliable sources where the known concentrations are in terms of parts per million by volume or mass per unit volume of sample gas. The use of this approach enables a check on the calculation as well as the accuracy of the analysis. The following procedure and criteria should be used:

a. Method 6: Analyze four samples at different levels of concentration. All four results should agree within $\pm$3.0 percent of the known concentrations.

b. Method 7: Analyze five samples at different levels of concentration. All five results should agree within $\pm$7.0 percent of the known concentrations.

Although the above criteria are more stringent than previously discussed, these lower limits are achievable as indicated in Table 7, and should be the goal of the analyst.

3. Periodically assess analytical accuracy.

a. Method 6: Analyze two audit samples (unknowns) concurrently with field samples. The results must agree within $\pm$5.0 percent of the audit concentrations on each of the two SO_2 audit samples.

b. Method 7: Analyze two audit samples (unknowns) concurrently with field samples. The results must agree within ±10.0 percent of the audit concentrations on each of the two NO_x audit samples.

References

1. Quality Assurance Handbook for Air Pollution Measurement Systems. Vol. III--Stationary Source Specific Methods. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/4-77-027b. August 1977. Sections 3.5.8 and 3.6.8.

2. Fuerst, R.G., R.L. Denny, and M.R. Midgett. A Summary of the Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7 - 1977. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/4-79-045. August 1979. 50 p.

3. Fuerst, R.G., and M.R. Midgett. A Summary of the Interlaboratory Source Surveys for EPA Reference Methods 5, 6, and 7 - 1978. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/4-80-029. May 1980. 48 p.

TABLE 1. SUMMARY OF TYPES OF ERRORS

	SO_2		NO_x		
Audit survey no.	0980	0281	0480	1080	0481
Reporting	0	0	1	0	1
Calculation	5	8	9	6	6
Analytical bias	33	39	23	26	25
Poor analytical precision	9	2	9	10	3
Poor calibration precision	-	-	-	-	7
Total no. of laboratories	99	117	69	66	58

TABLE 2. REPORTING ERROR EXAMPLE

EPA value	Reported value	% diff.	Corr. value	Corr. % diff.
497.7	480.0	- 3.6	-	-
696.8	678.0	- 2.7	-	-
119.5	119.0	- 0.4	-	-
895.9	290.3[a]	- 67.6	886.0	-1.4
298.6	886.0[a]	196.7	290.3	-2.8

[a] These two values were apparently interchanged.

TABLE 3. CALCULATION ERROR EXAMPLES

EPA value	Reported value	% diff.	Corr. value	Corr. % diff.
697.3	365.2[a]	-47.6[a]	730.4	4.7
298.7	147.1	-50.8	294.2	-1.5
896.5	454.0	-49.4	908.0	1.3
149.3	75.3	-49.6	150.6	0.9
498.0	253.4	-49.1	506.8	1.8
305.0	38.1[b]	-87.5[b]	280.5	-8.0
762.6	520.9	-31.5	763.3	0
1334.6	1106.1	-17.1	1348.5	1.0
1830.3	1564.2	-14.5	1806.6	-1.3
2287.8	2079.2	- 9.1	2321.6	1.5

[a] Reported values are apparently off by a factor of 2.

[b] Reported values are apparently off by a constant difference of 242.4.

TABLE 4. ANALYTICAL BIAS EXAMPLES

Sample	EPA value	Reported value	% diff.	Corr. value	Corr. % diff.
NO_x	746.6	812.5	8.8[a]	735.0	-1.7
	895.9	981.5	9.6	887.9	-1.0
	248.9	266.5	7.1	241.1	-3.5
	497.7	578.5	16.2	523.3	5.7
	99.5	110.5	11.0	100.0	0.5
SO_2	1143.9	1030.0	-10.0	1130.1	-1.2
	1906.5	1754.0	- 8.0	1924.5	-0.9
	762.6	698.0	- 8.5	765.9	0.4
	2287.8	2109.0	- 7.8	2314.0	1.1
	381.3	343.0	-10.0	376.3	-1.3

[a] There is an apparent analytical bias, possibly from the incorrect preparation of the potassium nitrate or barium standard.

TABLE 5. CALCULATION ERROR PLUS ANALYTICAL BIAS EXAMPLE

Sample	EPA value	Reported value	% diff.	Corr. value	Corr. % diff.
NO_x	497.7	58146.7[a]	11583.1[a]	499.5	0.4
	895.9	99926.3	11053.7	858.9	-4.2
	298.6	33940.5	11266.5	291.6	-2.4
	696.8	81836.2	11644.6	703.0	0.9
	119.5	14644.4	11540.5	125.8	5.3

[a] Reported values are apparently off by a factor of 100 with an analytical bias of about +14 percent.

TABLE 6. POOR ANALYTICAL PRECISION EXAMPLES

Calibration curve			Audit analysis				
Conc.	Abs.	% dev.	Sample	EPA value	Reported value	% diff.	Corr. % diff.
100	0.096	-50	NO_x	497.7	139.0	-72.1	-24.9
200	0.321	-16		696.8	234.0	-66.4	- 9.7
600	0.999	-13		119.5	62.9	-47.4	41.6
800	1.618	6		895.9	298.0	-66.7	-10.6
1000	2.205	15		298.6	115.0	-61.5	3.6
100	0.073	-14	NO_x	497.7	554.1	11.3	
200	0.147	-14		696.8	1010.8	45.1	
300	0.261	2		119.5	109.2	- 8.6	
400	0.349	2		895.9	1373.9	53.3	
				298.6	278.2	- 6.8	
			SO_2	305.0	320.0	4.9	
				762.6	764.8	0.3	
				1334.6	1192.9	-10.6	
				1830.3	1699.9	- 7.1	
				2287.8	2132.2	- 6.8	

TABLE 7. SUMMARY OF ANALYTICAL ACCURACIES

Survey 0980 (SO_2)	495 total analyses		450 analyses[a]			
≤ 2%	417	84%	405	90%		
≤ 3	437	88	418	93		
≤ 5	461	93	438	97		
Survey 0281 (SO_2)	585 total analyses		575 analyses[a]			
≤ 2%	485	83%	483	84%		
≤ 3	534	91	532	93		
≤ 5	560	96	558	97		
Survey 0480 (NO_x)	345 total analyses		300 analyses[a]			
≤ 7%	269	78%	260	87%		
≤ 10	292	85	280	93		
≤ 12	303	88	287	96		
≤ 15	306	89	290	97		
Survey 1080 (NO_x)	330 total analyses		280 analyses[a]			
≤ 7%	238	72%	224	79%		
≤ 10	274	83	256	91		
≤ 12	285	86	263	94		
≤ 15	295	89	266	95		
Survey 0481 (NO_x)	287 total analyses		272 analyses[a]		253 analyses[b]	
≤ 7%	238	83%	234	86%	217	86%
≤ 10	260	91	254	93	234	92
≤ 12	267	93	259	95	239	94
≤ 15	271	94	263	97	242	96

[a] Total analyses minus results from poor analytical precision.
[b] Total analyses minus results from poor calibration precision.